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# Valorization of carbon dioxide by co-electrolysis of CO<sub>2</sub>/H<sub>2</sub>O at high temperature for syngas production

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## Abstract

In order to reduce annual emissions of greenhouse gases, manufacturers are constantly trying to develop low-costly ways to treat carbon dioxide emissions from industrial activity. This can be done by valorizing the carbon dioxide (CO<sub>2</sub>) emitted by integrating it in production processes of other raw materials like chemicals or fuels. One such alternative should be the co-electrolysis of CO<sub>2</sub>/H<sub>2</sub>O at high temperature to produce syngas (H<sub>2</sub> and CO mixture), used for fuels elaboration or ethanol production. Electrolysis cell was modeled using Aspen Plus<sup>®</sup> V7.1 simulator and an economic evaluation was performed. It included investment and operating costs. The evaluated production cost for 1 kg of syngas would cost 1.30 €, which represents 69.27 €/GJ based on the low heating value for the considered syngas with a H<sub>2</sub>/CO ratio equal to 1.19.

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**Keywords:** Carbon Dioxide; Co-Electrolysis; High Temperature; Syngas; Solide Oxide Electrolysis Cell; Reverse Water Gas Shift; Simulation; Economic Evaluation;

## 1. Introduction

In the purpose of limiting temperature increase, we need to reduce global emissions of carbon dioxide (CO<sub>2</sub>), the main greenhouse gas. One of the possible options to achieve it is to capture and valorize the emitted CO<sub>2</sub>. The main issue is to find and to develop new applications using this molecule, while ensuring a favorable impact on the environment. The CO<sub>2</sub> could thus be used as feedstock in industrial processes, or through access to non-fossil energy, be transformed in a chemical or biological way to produce chemicals, pharmaceuticals and biofuels from the syngas production (mixtures of hydrogen and carbon monoxide) [1]. These two compounds are fundamental reactants for various productions of organic chemicals, like ethanol or synthetic fuels. In addition, hydrogen could become the main fuel and

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electricity source in the future. However, hydrocarbons, natural gas and petroleum fractions still remain the main source of syngas [2]. It can also be produced by fermentation of household waste, whose energy density is lower than that of natural gas. The syngas is obtained by reforming the methane abundantly present in the natural gas extracted from oil wells. However, syngas can also be produced from other carbon sources, such as coal by gasification.

One alternative to valorize the  $\text{CO}_2$  while producing valuable syngas is the use of an electrolyzer. This process consumes large volumes of  $\text{CO}_2$ . Its electrolysis can be carried out in different types of cells. This electrochemical way to valorize  $\text{CO}_2$  is a better alternative than carbon capture and storage (CCS), which can only avoid carbon emissions in the atmosphere without finding a real solution to valorize it [3]. However, very little experience feedback is the principle disadvantage. In a continuous context of development, we tend to explore all the potential of this new technology. The electrochemical conversion of  $\text{CO}_2$  will be performed by the use of carbon-free energies (such as solar or nuclear power) as a source of heat and/or electricity to allow the dissociation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (figure 1) by co-electrolysis [4].

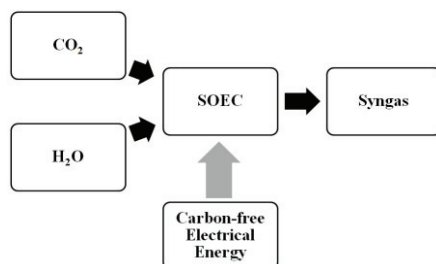


Fig. 1. Overall pattern for the electrochemical process production.

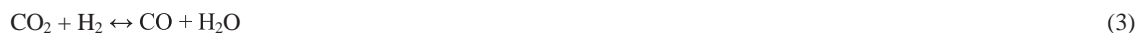
The conversion will be performed in a solid oxide electrolysis cell (SOEC). This cell is composed by three distinct and porous layers which represent two electrodes separated by an electrolyte as following:

- The cathode generally made of porous nickel, or a mixture of nickel and yttria stabilized zirconium (YSZ). The reduction reaction happens on this electrode surface
- The electrolyte, which allows the diffusion of the concerning ionic species ( $\text{O}^{2-}$  in this case). The solid electrolyte is also gas tight
- The anode, constituted by a mixture of lanthanide, strontium and manganese oxide (LSM) associated with YSZ material type. The anode is the oxidation electrode

Several electrochemical reactions take place in the SOEC compartments. Oxidation and reduction reactions are always present in any electrochemical reactions. For the co-electrolysis, water reduction reaction (1) and  $\text{CO}_2$  reduction reaction (2) occurs at the cathode interface as follows:



In addition to the electrochemical reaction, the conversion of  $\text{CO}_2$  is accompanied by an equilibrium reaction which is the reverse water gas shift (RWGS) described by the reaction (3):



RWGS can be the main production source of CO during the co-electrolysis, due to the favorable thermodynamic conditions [6]. The oxide ions formed by the reactions (1) and (2) migrate through the electrolyte, arrive at the anode surface, and are reduced into oxygen (O<sub>2</sub>) according to the reaction (3):



Electrolyzing at high-temperature is more efficient than running the electrolysis at low temperature for several reasons. In fact, working for example at a temperature of 1373 K can save 30% and 20% of the electricity need to reduce respectively CO<sub>2</sub> and water compared to an electrolysis at 373 K [7,8].

The syngas produced can be converted into synthetic fuel via Fisher-Tropsch reactions, or alcohols like ethanol via reactions with various products depending on operating parameters and used catalysts [9].

The objective of this paper is to model the production of syngas through the co-electrolysis of water and CO<sub>2</sub>. The numerical calculations used to estimate key parameters during electrolysis process will be detailed. The second step will be to design all the process on a simulator. Finally, an economic assessment will evaluate the cost of this type of syngas in comparison to usual syngas price.

## 2. Co-electrolysis model

The CO<sub>2</sub>/H<sub>2</sub>O co-electrolysis mechanism is complex, due to the described reactions that occurs simultaneously. Until now, it is not well established if the CO is mainly produced by electrolysis of CO<sub>2</sub>, or by the RWGS [10]. The co-electrolysis can be summarized as follows (reaction 5):



The second reaction that must also be taken into account is the RWGS (reaction (3)), a slightly endothermic reaction ( $\Delta H_{298\text{K}} = 41 \text{ KJ/mol}$ ). The main side reaction that can restrict the electrolysis progress is the coke formation (reaction (6)), or carbon deposit on the electrolyzer surface, as following:



Reaction (6) can take place if the cell voltage is large enough. Working with lower voltages avoids coke formation. Below 973 K with Ni as a catalyst, methane is formed according to the reaction (7).



Therefore we prefer to use temperatures above 973 K to prevent the formation of methane [11]. The electrolyzer will be run at a high temperature (1073 K), with an H<sub>2</sub>O/CO<sub>2</sub>/H<sub>2</sub> inlet molar ratio equal to 45/45/10 in order to minimize the internal resistance of cells [12].

### 2.1. Mass balance

The SOEC outlet composition depends on the temperature, current density applied on the cell, and the feed composition,. Note that the occurring electrochemical reactions are not really equilibrium reactions, since the sealing of solid electrolyte separate produced oxygen from the other species. The only equilibrium reaction is the RWGS (reaction (3)). In our model we consider that the CO<sub>2</sub> and H<sub>2</sub>O co-electrolysis passes through three stages. The first one is the RWGS, (reaction (3)), which takes place during the preheating of inlet gases at a temperature between 473 K and 573 K. The second step is the electrochemical reduction of CO<sub>2</sub> and H<sub>2</sub>O (reaction (5)) at 1073 K. The latter is a second step of RWGS (reaction (3)) at 1073 K, held at electrolyzer exit.

#### 2.1.1. The first RWGS step

Equation (8) shows the overall mass balance of the first RWGS taking into account all chemical compounds that contribute to the reaction and which are present at the feed stream.

$$n_0(H_2O) + n_0(H_2) + n_0(CO_2) + n_0(CO) = n_1(H_2O) + n_1(H_2) + n_1(CO_2) + n_1(CO) \quad (8)$$

Where  $n_0(H_2O)$ ,  $n_0(H_2)$ ,  $n_0(CO_2)$ , and  $n_0(CO)$  are respectively the inlet vapor molar fractions of  $H_2O$ ,  $H_2$ ,  $CO_2$ , and  $CO$ , while  $n_1(H_2O)$ ,  $n_1(H_2)$ ,  $n_1(CO_2)$ , and  $n_1(CO)$  represent the molar fraction of the same compounds after the first RWGS. The material balance is then performed for each chemical element, which are carbon (equation (9)), hydrogen (equation (10)), and oxygen (equation (11)):

$$n_0(CO_2) + n_0(CO) = n_1(CO_2) + n_1(CO) \quad (9)$$

$$2n_0(H_2O) + 2n_0(H_2) = 2n_1(H_2O) + 2n_1(H_2) \quad (10)$$

$$2n_0(CO_2) + n_0(CO) + n_0(H_2O) = 2n_1(CO_2) + n_1(CO) + n_1(H_2O) \quad (11)$$

The water gas shift reaction (the opposite of RWGS) is characterized by a constant of equilibrium  $K(T)$  (equation (12)) that involves the equilibrium mole fractions of the four chemical compounds:

$$K(T) = [n_1(H_2) \times n_1(CO_2)] / [n_1(H_2O) \times n_1(CO)] \quad (12)$$

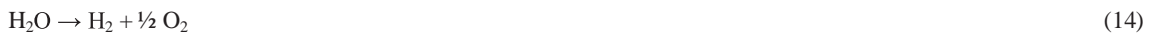
To evaluate the equilibrium constant depending of the local temperature  $T$  in K, we use an empirical relationship [13] shown by the equation (13) below to link the temperature  $T$  with the constant:

$$\log(K) = -2.4198 + 0.0003855 \times T + 2180.6/T \quad (13)$$

The resulting system has five equations (9)-(13) with five unknowns. It is therefore possible to solve it knowing the mole fractions at the entrance of the system for a given temperature.

### 2.1.2. Electrochemical reduction of $CO_2/H_2O$

The existing models for co-electrolysis are complex [14]. An iterative estimation is used, based on the estimated conversion rate of both reduction reactions of  $CO_2$  and  $H_2O$  (reactions (14) and (15)):



The conversion rates for both the reduction reactions of  $H_2O$  and  $CO_2$  are respectively noted  $X_{H_2O}$  and  $X_{CO_2}$ . An initial estimation is made on these values. Once outlet gas flowrates calculated, the output flowrates will be compared to results from the literature. If the relative errors between the experimental and calculated values are greater than 15%, new estimations of the conversion rates  $X_{CO_2}$  and  $X_{H_2O}$  are performed until the error meets the acceptance range. The values in the last iteration are retained.

### 2.1.3. The second RWGS step

The equilibrium composition is determined using the same equation system like in the first step, with only one difference: the oxygen balance must consider now the oxygen flowrate  $\Delta n(O_2)$  produced by reducing  $CO_2$  and  $H_2O$  (equation (16)) An index 2 will designate the outlet conditions after the electrochemical phase and an index 3 for the conditions after the second step of RWGS.

$$2n_3(CO_2) + n_3(CO) + n_3(H_2O) = 2n_2(CO_2) + n_2(CO) + n_2(H_2O) + \Delta n(O_2) \quad (16)$$

$\Delta n(O_2)$  can be calculated using equation (17):

$$\Delta n(O_2) = (I \times N_{cells}) / (2F \times Q_{gas}) \quad (17)$$

Where  $I$  (in A) is the electrical current in each cell,  $N_{cells}$  is the number of electrolysis cells,  $F$  (in C) is the Faraday constant, and  $Q_{gas}$  (in mol/hr) is the total molar flowrate of gas circulating through the SOEC.

## 2.2. Energy balance

Once the outlet gas composition is determined, the operating cell voltage is calculated using the Nernst potential ( $V_n$ ) law [11] (equation (18)):

$$V_n = -0.5F \times (\Delta G_{H_2O}(T) + RT \ln[(n_2(H_2O) \cdot P^{-1/2}) / (n_2(H_2) \cdot n_2(O_2)^{1/2} \cdot P_{std}^{-1/2})]) \quad (18)$$

Where:

- $V_n$  is the Nernst potential in V
- $\Delta G_{H_2O}$  is the Gibbs energy for  $H_2O$  formation in J
- $y_{H_2O}$ ,  $y_{H_2}$ , and  $y_{O_2}$  are respectively the gaseous molar fractions of  $H_2O$ ,  $H_2$  and  $O_2$  at the outlet of the electrochemical stage
- $P$  and  $P_{std}$  are respectively in MPa the applied pressure and the standard pressure (0.1013 MPa)

$V_n$  represents the standard equilibrium potential for the considered redox couples. However,  $V_n$  is not the applied potential of the cell. We have to consider the electrical losses. The electrical power leaking is led by an intrinsic SEOC characteristic which is the area specific resistance (ASR). It can be estimated using the Arrhenius equation (equation (19)) depending on a fixed initial ASR value at 1100 K:

$$ASR(T) = ASR_{1100K} - 0.463 + 3.973 \times 10^{-5} \exp^{(10300/T)} \quad (19)$$

Where  $ASR$  is the area specific resistance (in  $\Omega \cdot \text{cm}^2$ ), and  $T$  is the temperature in K.  $ASR_{1100K}$  is a user specified  $ASR$  at 1100 K [10]. With the existing technology, a value of  $1.25 \Omega \cdot \text{cm}^2$  can represents an achievable short term  $ASR$  for a stack assemblage of cells. Whereas a fixed value of  $0.25 \Omega \cdot \text{cm}^2$  is an optimistic value observed for button cells [11]. The voltage to apply follows the equation (20):

$$V_{op} = V_n + i \times ASR \quad (20)$$

Where  $V_{op}$  is the operating voltage (in V) in the cell, and  $i$  is the density current passing through the cell (in  $\text{A}/\text{cm}^2$ ).  $V_{op}$  consists of two compounds:

- A first term ( $V_n$ ) representing the theoretical voltage needed if the cell ideally works (Nernst potential)
- A second term ( $i \times ASR$ ) taking into account the electrical losses at SOEC level.

Knowing the operating voltage, the electrical power  $P_e$  (in kW) consumed in all the SOEC cells for the co-electrolysis is determined by the equation (21):

$$P_e = V_{op} \times i \times N_{cells} \quad (21)$$

## 2.3. Model validation

An algorithmic method is required to calculate the output parameters. Its steps are the following:

- The first step is to specify the values of operating parameters such as the inlet temperature, the current density and the flowrates of gas (with their composition) at the inlet
- Initial guess are made on the conversion rates  $X_{CO_2}$  and  $X_{H_2O}$  for the reactions (14) and (15). The iteration is then pursued until we reach a relative error below 15% (eq. 22)
- The gas composition at the exit is calculated based on mass balance equations

- The relative error  $err$  is estimated for each chemical species  $j$  relative to the results given by the literature using equation (22)

$$err(j) = 100 \times |v_{cal}(j) - v_{lit}(j)| / v_{lit}(j) \quad (22)$$

Table 1 represents our obtained results with other established results from the literature. The comparison concerned the calculations of Zhan et al. [15] and by O'Brien et al. [12]. The relative error, compared to the experiences of Zhan et al. does not exceed 6 %. As for the experience of O'Brien, the relative error is almost the double of this threshold (13%). This can be explained by the difference in the used equipment (e.g., type of electrode in the experiments, electrolyte main material) and the accuracy of the presumptions in both models. Note that the relative errors from our model are within the same range as other more complex models [6,15]. An ideal configuration should be obtaining errors under 10%. However, our results are quite acceptable and thus can be inputted for the process simulation.

Table 1. Output gas composition and the relative error obtained from iterative model.

Outlet gas	Our model	Zhan et al model [15]		O'Brien et al model [12]	
	Final composition (%)	Composition (%)	Relative error (%)	Composition (%)	Relative error (%)
CO <sub>2</sub>	19.2	17.0	5.7	24.7	13.0
CO	10.7	8.4	2.5	13.5	2.3
H <sub>2</sub>	52.5	55.2	3.2	48.1	7.0

### 3. Co-electrolysis simulation

#### 3.1. Simulator

Aspen Plus<sup>®</sup> is a widely used software in chemical engineering to model and size industrial processes. However, Aspen Plus<sup>®</sup> does not contain a prebuilt electrolyzer. Therefore we will use our model to design the electrolyzer as a combination of prebuilt units in Aspen Plus<sup>®</sup>. The two step RWGS will be simulated in *REquil* reactors, a prebuilt reactor type in Aspen Plus<sup>®</sup> that model equilibrium reactions. Regarding the two electrochemical reduction of CO<sub>2</sub> and H<sub>2</sub>O, they will be simulated using a reactor called *RStoic*, which is a reactor based on known and fixed conversion rates of reactants. These conversion rates will be set to the output values obtained from our model, with  $X_{CO_2} = 0.05$  and  $X_{H_2O} = 0.98$ .

#### 3.2. Process description

The reactants required for co-electrolysis, which are water, carbon dioxide and dihydrogen are conditioned before entering the cell:

- The water is brought under ambient conditions (atmospheric pressure and 298 K temperature).
- The CO<sub>2</sub> comes from transporting the CO<sub>2</sub> in supercritical form, typically at 15 MPa [17].
- The hydrogen is retrieved from stored H<sub>2</sub> in special pressurized tankers of 10 MPa.

Working with a H<sub>2</sub>O/CO<sub>2</sub>/H<sub>2</sub> molar ratio equivalent to 45/45/10, the flowrates of H<sub>2</sub>O, CO<sub>2</sub> and H<sub>2</sub> are set respectively to 450 kmol/hr (8107 kg/hr), 450 kmol/hr (19804 kg/hr) and 100 kmol/hr (202 kg/hr).

The gases are brought down to atmospheric pressure with valves VLV1 VLV2 and then heated (HX1 and HX2) to 473 K (figure 2). Demineralized water is also heated (HX3) to attain the same temperature. The three inlet streams are mixed and passes through the first reactor (LRWGS), where occurs the low

temperature step of RWGS. This reactor is heated so that the temperature at the outlet reaches (573 K). The outlet flow is heated until reaching the electrolysis temperature (HX4) and then electrochemically reduced in a second reactor (ELECTRO), where gaseous oxygen is formed. A simple component separator (YSZ-ELEC) allows splitting the flow in two streams. One stream is a pure oxygen flow, and the other one enter the last equilibrium reactor (HRWGS) to achieve the second step of RWGS.

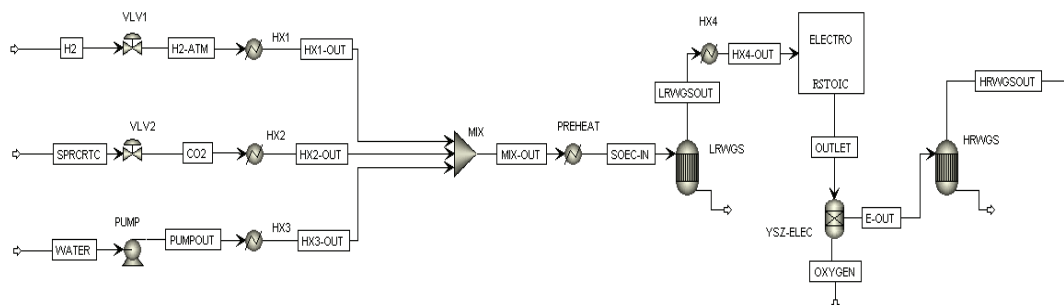


Fig. 2. Syngas production flowsheet.

### 3.3. Simulation results

Although Aspen Plus<sup>®</sup> is a powerful software, it does not incorporate the notion of electrical energy requirement for reactions (electrochemical conversions). However, a rudimentary calculation can be done to estimate the electrical power needed to reduce CO<sub>2</sub> and water, based on thermodynamic variables. In fact, Aspen Plus<sup>®</sup> outputs a duty value that represents the required enthalpy for the reaction ( $\Delta H$ ). This enthalpy has two components: an electricity need ( $\Delta G$ ), and a thermal demand ( $T\Delta S$ ). The total enthalpy  $\Delta H$  is given by the net heat duty flowing into the reactor ELECTRO.  $\Delta S$  is easily estimated because the software provides entropy values upstream and downstream the ELECTRO reactor. Knowing total and energy need, electrical requirement is calculated. Table 2 summarizes all the energy need in the process.

Table 2. Energy power consumption for each process unit.

Process unit	Thermal power consumption (kW)	Electrical power consumption (kW)
HX1	240.72	-
HX2	2307.36	-
HX3	6355.69	-
HX4	6061.10	-
PREHEAT	1.09	-
LRWGS	1118.96	-
HRWGS	2194.59	-
ELECTRO	484.50	35130.50
Total	19514.54 <sup>a</sup>	35130.50

<sup>a</sup> After assuming 4% of thermal losses.

Even if electrical consumption is only localized at the level of the electrolyzer, it nevertheless represents 62% of the total energy consumption. The electricity represents a significant part of total operating costs. The heat exchangers HX3 (used to generate hot low pressure steam) and HX4 require the highest thermal demand. This heat can be partially provided by the hot process streams leaving the reactors. The outlet cooling (not represented in the flowsheet) required to remove the formed water after



the HRWGS can achieve that task. Another alternative to provide more heat is to cool down the oxygen produced at the anode for further easier low temperature storage.

With our initial feed flows, we produce 616.67 kgH<sub>2</sub>/hr and 7276.88 kgCO/hr in a H<sub>2</sub>/CO molar ratio of 1.19. However, the net production for hydrogen is lowered to 415.08 kgH<sub>2</sub>/hr due to the 100 kmolH<sub>2</sub>/hr in the feed stream that is consumed during the electrolysis process (RWGS steps).

#### 4. Economic evaluation

The economic evaluation of a process is always approximate. This is due to the costs of raw materials, energy (electricity), and facilities that vary over time and technological progress. It is assumed that the total production cost of synthesis gas will depend on two types of costs: investment cost (installation cost) and operating costs (energy and material consumption).

##### 4.1. Considered hypotheses

The following assumptions are made to evaluate the total process cost:

- The whole SOEC contains 20 cells with an 834 cm<sup>2</sup> active area per cell based on Siemens-Westinghouse technology [18].
- The total power consumption is spread on cells with a unitary working power equal to 110 W [18].
- The current density should be between -0.3 and -1.2 A/cm<sup>2</sup> in order to minimize battery aging and to preserve an SOEC lifespan over 5 years [4].
- The applied pressure in the SOEC is atmospheric.
- The inlet gas molar composition (in percentage) is: 45% H<sub>2</sub>O, 10% H<sub>2</sub>, 45% CO<sub>2</sub> [12].
- Under these conditions, the ASR is 2.12 Ω.cm<sup>2</sup>.

##### 4.2. Investment costs

They can be estimated based on the active surface of the cells (€/m<sup>2</sup>). The stack investment expense concerning the cost per surface unit is set to 5140 €/m<sup>2</sup> [19]. Due to the lack of feedback for this type of equipment, installation costs for each necessary unit composing the process will not be considered. The installation and maintenance of the electrochemical system also requires significant funding at an average of 4080 €/m<sup>2</sup> of SOEC area [4]. However, this investment is more amortized over the period view that the lifespan of the whole process (20 years) is higher than that of the SOEC. This means that the electrolyzer will need to be renewed several times during the process functioning. However, cell replacement cost is not considered due to the weak accuracy and standardization for this kind of procedure.

##### 4.3. Operating costs

These costs include raw material price (CO<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub>), plus the electrolyzer energy consumption cost. The considered cost of CO<sub>2</sub> capture is 24 €/ton, which is the mean cost for capturing CO<sub>2</sub> from atmospheric emissions [4]. The water cost (demineralized water) is 0.87 €/m<sup>3</sup>, which corresponds to a desalinated sea water production cost [4]. Regarding the total energy consumption expense, it is the sum of electrical consumption (76.3 €/MWhr) plus the thermal energy consumption provided by renewable energy electricity generation (22.9 €/MWhr), with a thermal energy to electrical energy conversion factor of 0.3 in France [20]. Thermal losses are considered at each heater level to meet the reality in heat exchanging. The heat leaking represents 4% of a concerned heat flow. In addition, due to the irregularity power production of renewable energy, a process availability of 60% is assumed to represent periodic



dead time production. However, this availability depends on the type of considered renewable energy that will power the SOEC. Table 3 summarizes all the operating parameters:

Table 3. Principle operating parameters adopted for the syngas production process.

Operating parameters	Value
Electricity price	76.3 €/MWhr
Thermal energy cost	22.9 €/MWhr
Demineralized water price	0.87 €/m <sup>3</sup>
CO <sub>2</sub> capture cost	24 €/ton
Thermal losses	4%
Energy availability	60%
Operating and maintenance	0.41 €/GJ fuel <sup>a</sup>

<sup>a</sup> Per GJ of produced fuel based on syngas low heating value (LHV). LHV(H<sub>2</sub>) = 120.09 MJ/kg, LHV(CO) = 10.16 MJ/kg

#### 4.4. Syngas production cost

Assuming the previous operating and investment costs, and taking an € to US \$ exchange rate of 1.226 (average exchange rate in July 2012), the final syngas production cost is 1.30 €/kg, which also represents 69.27 €/GJ based on the low heating value (LHV) of H<sub>2</sub> and CO. Production cost of hydrogen generally varies between 0.58 €/kg (hydrogen obtained by steam reforming) and 3.60 €/kg (alkaline electrolyzer for H<sub>2</sub> production) [21]. Concerning the CO, the costs of production vary according to the adopted process type for CO production (e.g. dry reforming, cryogenic way) between 1.30 €/kg and 6.53 €/kg [22]. Assuming the same H<sub>2</sub>/CO molar ratio of 1.19 like the ratio obtained in the simulation, the average range production price is thus between 1.24 €/kg and 6.30 €/kg. Our syngas is located within this range of price. Nevertheless, its value is closer to the lower values of production costs (reserved for the widespread present processes) while it should be normally located near the upper bound (the case of under developing processes). In addition, a production cost like 1.30 €/kg is quite low, because the process does not take into account the presence of a CO<sub>2</sub> capture unit (i.e. by chemical absorption due to the low CO<sub>2</sub> partial pressure) situated after the SOEC outlet. A capture process would require higher operating costs (e.g. reboiling power, solvent consumption) and other investment costs associated to the installation of absorber and regenerating columns. Moreover, the only losses that were considered in the electrolyzer are by heat leaking. However, electrical losses, mainly by Joule effect, should be related to the SOEC. These losses will be proportional to the actual ASR inside the SOEC.

Syngas production by electrolysis offers the possibility to produce a clean syngas (assuming that the electricity comes from a carbon-free energy source) but at the expense of higher production costs, mainly due to the share of installing stack (figure 3). This constraint hampers the new syngas production method. The electricity share is nearly the quarter of the total syngas production cost, which is very significant. The efficiency of the syngas production is really dependent to the electricity price considered at that time. However, this percentage might diminish in the coming years due to the constant decrease in the MWhr price over time.

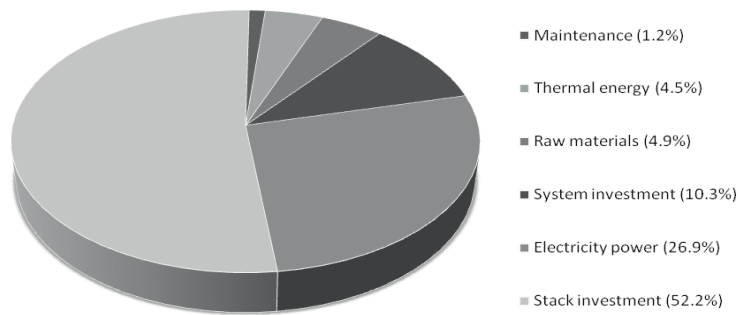


Fig. 3. Syngas production total cost distribution by sector of expenses.

It is legitimate to compare those production costs with a more conventional energy source that is the most widespread used today; oil. A comparison is performed between 1 kg of syngas with a  $H_2/CO$  molar ratio of 1.19 and 1 kg of oil. The assumed ton equivalent oil (toe) is issued by the International Energy Agency (IEA), with an average of 41.868 GJ/ton (the LHV depends on oil composition) [23]. A ton of oil can represent between 7 and 10 barrels of oil depending on oil density (according to the oil well origin). With a barrel price varying in the last seven years between 70 \$ (low bound), and a maximum price about 145 \$ (price rise in 2008), the oil price range is between 10 and 28 €/GJ [24]. The produced syngas has a price that is well outside this range. A high syngas production cost represents the main constraint for the electrochemical production of syngas. Indeed, from figure 5, the power consumption share is large enough for this new type of production, making the process less efficient. In addition, technologies used for electrolysis are still highly expensive. The total SOEC investment represents more than half the expenses for syngas production. This is due to the obvious lack of commercialization of electrolysis apparatus and also because SOEC are still under validation steps in laboratories.

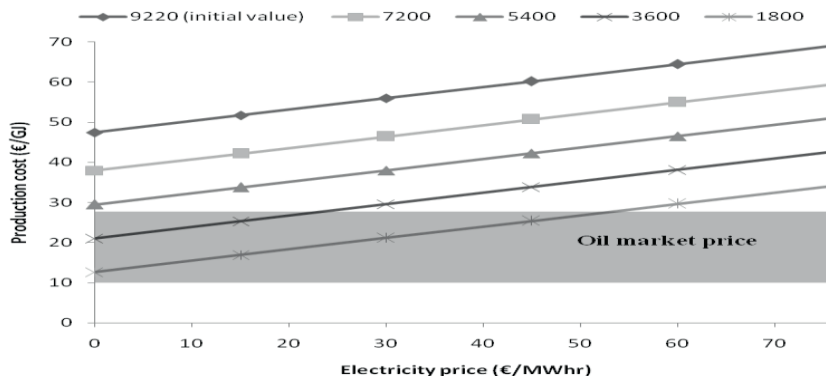


Fig. 4. Effect of electricity price depreciation over time on the syngas production cost for different values of investment per surface (in €/m²).

The two major expenditure areas during the syngas production are investment cost and electric consumption. A sensitivity analysis has been carried out by integrating these two parameters. This assessment was made in order to estimate the process feasibility in the future when the costs will become more affordable. For an initial investment of 9220 €/m² like in our treated case (figure 4), we note that even while assuming to consume a free electricity, expenses related to syngas production are still largely higher than crude oil price. By varying the investment costs to lower values, the shortfall margin is

reduced until the prices are within crude oil price range. It will be reachable when the total investment cost becomes lower than 40% of the initial investment cost. This reduction may seem quite excessive for short term, but possible in a decade or two with the constant progress made in SOEC technology. The syngas produced by co-electrolysis is also conceivable if electricity prices fall too, to nearly 50 €/MWhr. This fall depends on oil barrel price but also on changes in world asks and bids of electricity. The electrolysis syngas have to be at least within this range because the main interest is to produce synthetic fuel (e.g. gasoline, diesel). With this extra step, more costs due to Fischer-Tropsch reactions leading to synthetic fuels have to be taken into account. Syngas might be produced with the possible lowest cost. But even if electricity and investment costs reach the crude oil barrel price interval, the notion of profit should be considered too. Indeed, the interval shown in figure 4 is the market price of crude oil, not its production cost. This is due to the presence of petroleum revenue taxes that are applied by governments in order to manage national oil consumption. The production cost varies between 40% and 70% of the crude oil market price depending on governmental policies [25]. So a consequent margin should also be taken into account for syngas commercialization. The margin purpose is generating benefit that would make synthetic fuels as much competitive as oil. All of the cited constraints make the production of synthetic fuels starting with SOEC co-electrolysis not yet predictable for the very next years.

## 5. Conclusions

This study aimed to build simulative approaches dealing with syngas production via an electrochemical way. The new alternative is the co-electrolysis of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at high temperature in SOEC for a better conversion rate. This technique offers several other advantages. The most important asset is that it can valorize  $\text{CO}_2$ , the main greenhouse gas emitted by industrial activity. This chemical valorization is a serious alternative to a simple  $\text{CO}_2$  underground storing. Moreover, the co-electrolysis using electricity from renewable energy will represent a syngas production mode cleaner than current processes (steam reforming). However, this technology is still under development. It requires more improvements, such as a cell area amelioration, improvement in SOEC lifespan, and catalyst stability enhancement. These parameters will reduce investment costs by increasing the electrolyzer performance.

The first estimations made on the syngas production cost shows that the cost is around 1.30 €/kg of produced syngas, converted to 69.27 €/GJ based on the low heating value of  $\text{H}_2$  and  $\text{CO}$ . This cost is not yet competitive with the crude oil price, which is between 10 €/GJ and 28 €/GJ. However, more research in this area will substantially reduce the investment costs that limit the competitiveness of syngas recovered from  $\text{CO}_2$ . This objective would also be achieved when the price of electrical MWhr become more affordable. However, the economic evaluation is slightly incomplete. Different other parameters have to be taken into account to improve the economic estimation. A  $\text{CO}_2$  capture unit placed after the electrochemical process, more based on chemical absorption due to the low  $\text{CO}_2$  partial pressure, should be designed. The power needed to regenerate the extracting solvent added to the installation cost will reduce process efficiency and thus make the syngas price more expensive. A better energy integration will also reduce the expenses related to the heat consumption. All the previously listed improvements would be achievable for midterm.

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